

- (16) J. H. Baxendale and D. T. Westcott, *J. Chem. Soc.*, 2347 (1959); M. G. Vladimirova and I. A. Kahovskii, *Zh. Prikl. Khim. (Leningrad)*, **23**, 580 (1956); R. M. Izatt, H. D. Johnston, G. D. Watt, and J. J. Christensen, *Inorg. Chem.*, **6**, 133 (1967); E. A. Simpson and G. M. Waind, *J. Chem. Soc.*, 1746 (1958).
- (17) In some places Cu(AO) will be used to describe the starting complexes and Cu(AO)CN the initial product.
- (18) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).
- (19) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).
- (20) Large spectral changes occur: $\epsilon_{\max}(520 \text{ nm}) \rightarrow \epsilon_{\max}(620 \text{ nm})$ with two isobestics.
- (21) The kinetic value for K_2 is 4.3 M^{-1} for Cu(EnAO-2H) $(\text{CN})_2^{2-}$ to be compared with $5 \times 10^4 \text{ M}^{-1}$ for K_1 (at 20°C).
- (22) N. Guyeth and T. H. Matthes, *Acta Chem. Scand.*, **28**, 13 (1974).
- (23) A closely related study on the spectral and formation constants of CN^- adducts to tri- and tetradentate ligand-Cu(II) complexes has appeared since submission of this paper. This study is in agreement with the results presented here. See F. J. Billo, *Inorg. Nucl. Chem. Lett.*, **13**, 673 (1977).

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Kinetics and Mechanism of Oxidations by Peroxodiphosphate. 6. Copper(II)-Catalyzed Oxidation of Iodide

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Copper(II)-catalyzed oxidation of iodide with peroxodiphosphate (Perox) has been carried out at $I = 0.5 \text{ M}$ and at 30, 35, 40, and 45°C . The results conform to the rate law $-d[\text{Perox}]/dt = k_0[\text{Perox}][\text{H}^+] + k_c'[\text{Perox}][\text{Cu}^{\text{II}}]^2[\text{I}^-]/[\text{H}^+]$, where $k_0 = (k_1'[\text{I}^-] + k_2')$. The first term corresponds to the uncatalyzed reaction, and k_c' is a complex rate constant for the catalyzed path. k_0 values (at $[\text{I}^-] = 0.1 \text{ M}$) were $(7.1 \pm 0.2) \times 10^{-3}$, $(11 \pm 2.2) \times 10^{-3}$, and $(22 \pm 2) \times 10^{-3} \text{ s}^{-1}$ at 30, 35, and 45°C , respectively, and compare well with the values found earlier for the uncatalyzed reaction. k_c' values were $(25 \pm 1) \times 10^5$, $(40 \pm 2) \times 10^5$, and $(70 \pm 5) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 30, 35, and 45°C , respectively. Copper(II) catalysis operates through complex formation of Cu^{II} with peroxodiphosphate. Moderately concentrated solutions of Cu^{II} and peroxodiphosphate yield a blue precipitate which has these reactants in the ratio 2:1. Spectrophotometric results also suggest complex formation, but there is no kinetics evidence.

The interest in the oxidations by peroxodiphosphate has been of recent origin. Though the oxidation potential of peroxodiphosphate is 2.07 V, it is kinetically inhibited and not much work has been done so far. In most kinetics studies,¹⁻³ the mechanism involves a rate-determining hydrolytic path. The oxidation^{4,5} of iodide is one in which the mechanism is more complicated and also involves a direct reaction between the oxidant and reductant. An iodometric determination⁶ of peroxodiphosphate employing copper(II) as catalyst has also been reported. The present paper describes a detailed kinetics study of this catalysis and the mechanism of reaction. The role of copper(II) in peroxodiphosphate oxidations is not yet known and this is perhaps the first reaction in which it has been reported. It would be worthwhile to know whether a $\text{Cu}^{\text{II}}\text{-Cu}^{\text{I}}$ cycle operates or whether copper(II) lowers the energy barrier by complex formation with any or both of the reactants. A possibility of both processes is also not ruled out.

Experimental Section

Materials. Tetrapotassium peroxodiphosphate $\text{K}_4[\text{P}_2\text{O}_8]$ was a gift from FMC Corp. Potassium phosphate and potassium fluoride present as impurities had no effect on the kinetics of the reaction, and hence the sample was used as such. Its solution was prepared by direct weighing and standardized cerimetrically⁷ and iodometrically.⁶ The two results were similar. Potassium iodide and copper sulfate were BDH (AnalaR) grade. The perchloric acid was 70% AnalaR Riedel. All other chemicals employed were either BDH (AnalaR) or Merck quality. Doubly distilled water was used for preparing all solutions, the second distillation being from permanganate.

Kinetic Procedure. Iodide, perchloric acid, and other constituents in the desired amounts were taken in a reaction vessel and thermostated at $35 \pm 0.1^\circ \text{C}$ unless otherwise mentioned. A calculated amount of sodium thiosulfate and some starch solution were also added. The reaction was initiated by adding the temperature-equilibrated peroxodiphosphate to the reaction vessel. The iodine liberated reacts with the thiosulfate and the blue color does not appear till the thiosulfate is used up. The time for the appearance of blue color was noted and immediately more of the calculated amount of thiosulfate was added. The process was repeated with decreasing amounts of thiosulfate until 3 half-lives of the reaction were over.

A preliminary study indicated that no reaction occurs between peroxodiphosphate and thiosulfate, if their concentrations are of the same order of magnitude as in the reaction mixture. Similarly starch

did not interfere with the kinetics. Small amounts of tetrathionate had no effect on the rate of reaction. No precipitate of cuprous iodide was visible in the reaction mixture. First, the concentration of Cu^{II} employed was small. Second, even if Cu^{I} is formed, it would almost immediately be oxidized by peroxodiphosphate yielding copper(II). A few reactions in acid medium, studied with conventional procedures, showed that if copper(I) and peroxodiphosphate are 1×10^{-3} and $5 \times 10^{-4} \text{ M}$, respectively, the reaction between them is completed in less than the time of rapid mixing, i.e., 2 s at 25°C . Copper(II) was estimated by noting its absorbance at 710 nm.

Since an equivalent amount of iodide is obtained back from the reaction of iodine and thiosulfate, the concentration of iodide was always constant during a run and the results were pseudo first order for all concentrations of iodide. Hence, pseudo-first-order rate constants were calculated from the straight-line plots of $\log [\text{Perox}]$ vs. time. The results were reproducible to $\pm 5\%$.

pH titrations of peroxodiphosphate, with perchloric acid at 35°C and ionic strength (LiClO_4) of 0.5 M, were made on an Expand pH meter from Electronic Corp. of India. These measurements yielded the third and fourth dissociation constants of peroxodiphosphoric acid under the desired conditions.

Spectrophotometric measurements were made on a Beckman DU spectrophotometer using 1-cm cells to determine complex formation between peroxodiphosphate and copper(II) and between iodide and copper(II). A determination of the formation constants was not possible because there is weak complexing and the complexes are not characterized.

A complex of copper(II) and peroxodiphosphate was prepared by mixing concentrated solutions in the absence of any acid. The resulting light blue precipitate was filtered, washed, and dissolved in the least amount of perchloric acid. Copper(II) content was determined iodometrically, and peroxodiphosphate content was determined cerimetrically.

Results

Peroxodiphosphate Dependence. The concentration of peroxodiphosphate was varied in the range $(0.85\text{--}42.5) \times 10^{-3} \text{ M}$ with fixed $[\text{KI}] = 0.1 \text{ M}$, $[\text{HClO}_4] = 0.1 \text{ M}$, and $[\text{Cu}^{\text{II}}] = 1 \times 10^{-5} \text{ M}$ at 35°C . In all cases plots of $\log [\text{Perox}]$ vs. time yielded straight lines. The average value of the pseudo-first-order rate constant (k_{obsd}) was found to be $(17.4 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$. These results are given in Table I.

Copper(II) Dependence. The concentration of copper(II) sulfate was varied in the concentration range $(1\text{--}50) \times 10^{-6}$

Table I. Peroxidodiphosphate Dependence in the Copper(II)-Catalyzed Oxidation of Iodide: Pseudo-First-Order Rate Constants k_{obsd} at 35 °C and $I = 0.5 \text{ M}^a$

$10^3 \times$ [Perox]/ M	$10^4 k_{\text{obsd}}/$ s^{-1}	$10^3 \times$ [Perox]/ M	$10^4 k_{\text{obsd}}/$ s^{-1}
0.85	17.6	17.00	17.6
1.70	18.5	21.25	16.4
3.40	16.4	25.50	17.6
5.10	17.1	29.75	17.6
6.80	17.6	34.00	16.4
8.50	17.6	42.50	17.1
12.75	18.6		

^a $[\text{HClO}_4] = 0.1 \text{ M}$; $[\text{KI}] = 0.1 \text{ M}$; $[\text{Cu}^{\text{II}}] = 1 \times 10^{-5} \text{ M}$. ^b Average = 17.4 ± 0.3 .

M at four temperatures and three different hydrogen ion concentrations. The observed pseudo-first-order rate constants and those calculated from eq 10 are given in Table II. Plots of these rate constants vs. $[\text{Cu}^{\text{II}}]$ yield curves with intercepts showing that there must be a term in the rate law independent of $[\text{Cu}^{\text{II}}]$ corresponding to the uncatalyzed reaction. Intercepts for $[\text{Perox}] = 8.5 \times 10^{-3} \text{ M}$, $[\text{KI}] = 0.1 \text{ M}$, and $[\text{HClO}_4] = 0.5 \text{ M}$ were found to be 40 ± 2 and 96 ± 4 at 35 and 45 °C, respectively, and for $[\text{HClO}_4] = 0.1 \text{ M}$, these values were 9.5 ± 1 and 20 ± 3 at 35 and 45 °C, respectively. The corresponding values for the observed rate constants from the uncatalyzed study⁵ are 49 and 103 and 7.0 and 23. The agreement in these values is satisfactory. A plot of k_{obsd} vs. $[\text{Cu}^{\text{II}}]^2$ yields a straight line with an intercept. The rate law must, therefore, be of the form

$$k_{\text{obsd}} = A + B[\text{Cu}^{\text{II}}]^2 \quad (1)$$

where A and B are terms including rate constants and iodide and hydrogen ion dependences.

Iodide Dependence. The concentration of iodide was varied in the range $(1-250) \times 10^{-3} \text{ M}$ at four temperatures and at

fixed $[\text{H}^+] = 0.1 \text{ M}$ and $[\text{Cu}^{\text{II}}] = 1 \times 10^{-5} \text{ M}$. The results are given in Table III. A plot of k_{obsd} vs. $[\text{I}^-]$ yields a straight line with an intercept. It is obvious that the rate law must have a term independent of iodide concentration. The form of the rate law is (2), where C and D are complex rate

$$k_{\text{obsd}} = C + D[\text{I}^-] \quad (2)$$

constants including copper(II) and hydrogen ion dependences. The term independent of iodide refers to the slow step of hydrolysis of peroxidodiphosphate and has been found in the uncatalyzed reactions^{4,5} also.

Hydrogen Ion Dependence. Hydrogen ion dependence was studied by varying the concentration of perchloric acid in the range 0.025–0.25 M, and the ionic strength was adjusted with lithium perchlorate. The results are shown in Table IV. A plot of k_{obsd} vs. $[\text{H}^+]$ yields a curve. A plot of $k_{\text{obsd}} [\text{H}^+]$ vs. $[\text{H}^+]^2$ yields a straight line with an intercept. The values of $[\text{H}^+]$ were calculated by subtracting twice the concentration of peroxidodiphosphate from the concentration of perchloric acid. Thus, the form of the rate law showing hydrogen ion dependence is (3), where P and Q are complex rate constants

$$k_{\text{obsd}} = P[\text{H}^+] + Q/[\text{H}^+] \quad (3)$$

involving Cu(II) and iodide dependences. From the hydrogen ion dependence of the uncatalyzed study,³ the first term on the right-hand side of eq 3 should correspond to the rate constant of the uncatalyzed path. The second term, therefore, must correspond to the catalyzed path.

Other Effects. There was no effect of the variation of ionic strength (lithium perchlorate) on the rate of reaction. No decrease in the rate was observed in the presence of small amounts (0.001–0.01 M) of dihydrogen phosphate.

Discussion

The peroxidodiphosphate ion has a charge of 4– and the third and fourth acid dissociation constants of peroxidodiphosphoric acid are reported⁸ to be 6.6×10^{-6} and 2.1×10^{-8} at 25 °C.

Table II. Copper(II) Dependence in the Oxidation of Iodide with Peroxidodiphosphate: Pseudo-First-Order Rate Constants k_{obsd} ($\text{s}^{-1} \times 10^{-4}$)^a

$10^5 [\text{Cu}^{\text{II}}]/$ M	$T, [\text{HClO}_4]$							
	45 °C, 0.5 M	45 °C, 0.1 M	40 °C, 0.1 M	35 °C, 0.5 M	35 °C, 0.1 M	30 °C, 1.0 M	30 °C, 0.5 M	30 °C, 0.1 M
0.1						47.5 (71)	23.5 (23.5)	6.5 (7.3)
0.4		25 (23)	15.7					7.6 (8.1)
0.5	98 (110)			42 (57)		50 (71)	26 (35.6)	
0.6					13 (12.4)			
0.8					15.5 (13.6)			
1.0	103 (111)	28 (29)		42.5 (56)	17 (15)	52 (71)	33 (36)	10.3 (9.6)
1.5		42.5 (38)			23.5 (20)			13.7 (12.7)
2.0	108.5 (115)		40	46 (58)	28 (27)	57 (72)		19 (17)
2.5		65.5 (65.7)						21 (23)
3.0	127 (122)	87.5 (85)		55 (62)	49.5 (49)	65 (73)	42 (40)	34 (30)
3.5		106 (108)			65 (60)			38 (38)
4.0	147 (132)	124 (134)	89	66 (68)	76 (75)		44 (43)	51 (47)
4.5					87.5 (88)			61 (58)
5.0	198 (197)		122	72 (75)	102.5 (111)	84 (77)	52 (47.5)	67 (69.5)

^a $[\text{Perox}] = 8.5 \times 10^{-3} \text{ M}$; $[\text{KI}] = 0.1 \text{ M}$. Figures in parentheses are calculated values from eq 10 using average $(k_1'[\text{I}^-] + k_2')$ values of 7.1×10^{-3} , 11×10^{-3} , and $22 \times 10^{-3} \text{ s}^{-1}$ and average k_c' values of 25×10^5 , 40×10^5 , and $70 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 30, 35, and 45 °C, respectively.

Table III. Iodide Dependence in the Copper(II)-Catalyzed Oxidation of Iodide with Peroxodiphosphate: Pseudo-First-Order Rate Constants k_{obsd} at 35 °C and $I = 0.5 \text{ M}^a$

[KI]/M	$10^4 k_{\text{obsd}}/\text{s}^{-1}$			
	30 °C	35 °C	40 °C	45 °C
0.001		0.76		
0.0025		1.7	2.0	
0.005	1.9	3.05	4.2	5.1
0.010	2.05	4.2		7.6
0.025	3.05	6.1	7.6	10.8
0.050	5.3	8.0	9.1	17
0.075	9.5	11.5	14.1	26
0.100	13.7	16	18	30
0.150	18	20	29	51
0.200	23	24	38	
0.250	26	33	47.5	

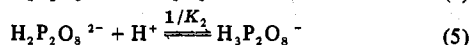
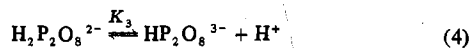
^a [Perox] = $8.5 \times 10^{-3} \text{ M}$; [HClO₄] = 0.1 M; [Cu^{II}] = $1 \times 10^{-5} \text{ M}$.

Table IV. Hydrogen Ion Dependence in the Copper(II)-Catalyzed Oxidation of Iodide with Peroxodiphosphate: Pseudo-First-Order Rate Constants k_{obsd} at 35 °C and $I = 0.5 \text{ M}^a$

[HClO ₄]/M	$10^4 k_{\text{obsd}}/\text{s}^{-1}$		
	30 °C	35 °C	45 °C
0.025			22 (33)
0.050	8.4 (8.5)	12.5 (13.5)	23.5 (25)
0.075	9.5 (8.6)	13.5 (13.5)	25.0 (26)
0.10	11.5 (9.6)	16.5 (15)	27.5 (29)
0.15	12.7 (12.2)	17.0 (19)	32.0 (37.7)
0.20	15.6 (15.4)	21.0 (24)	43.0 (47.5)
0.25	18.0 (19)	22.5 (29)	54.5 (58)
0.30	22.0 (21.8)	27.0 (34)	62.0 (68)
0.40	30.0 (29)	34.0 (45)	83.0 (89)
0.50 ^b	37.0 (36)	42.0 (56)	102.5 (111)

^a [Perox] = $8.5 \times 10^{-3} \text{ M}$; [KI] = 0.1 M; [Cu^{II}] = $1 \times 10^{-5} \text{ M}$. Figures in parentheses are k_{obsd} 's calculated from eq 10 using average ($k_1'[\text{I}^-] + k_2'$) values of 7.1×10^{-3} , 11×10^{-3} , and $22 \times 10^{-3} \text{ s}^{-1}$ and average k_c' values of 25×10^5 , 40×10^5 , and $70 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 30, 35, and 45 °C, respectively. ^b Ionic strength was 0.6 mol dm⁻³.

These values were redetermined by pH titrations at $I = 0.5 \text{ M}$ (lithium perchlorate) and at 35 °C and were found to be 3.33×10^{-5} and 1.3×10^{-6} , respectively. Crutchfield and Edwards⁸ have estimated the first and second dissociation constants also, but the method was shown to be in error by Venturini et al.⁹ Subsequently, in the oxidation of bromide² it was concluded that the second acid dissociation constant is at least 40 and the first one is larger than 40. From these results it is obvious that the peroxodiphosphate species mainly present (>95%) in the acid solutions employed is $\text{H}_2\text{P}_2\text{O}_8^{2-}$ and the two other species, present in small proportions, are correlated with it as in equilibria 4 and 5, where K_2 and K_3



are the second and third acid dissociation constants. From the hydrogen ion dependence it appears that though $\text{H}_2\text{P}_2\text{O}_8^{2-}$ is the predominant species, the reactive species are $\text{HP}_2\text{O}_8^{3-}$ and $\text{H}_3\text{P}_2\text{O}_8^-$. With the values of K_2 and K_3 mentioned above, their concentrations are given by (6) and (7), where [Perox]_T

$$[\text{HP}_2\text{O}_8^{3-}] = K_3 [\text{Perox}]_T / [\text{H}^+] \quad (6)$$

$$[\text{H}_3\text{P}_2\text{O}_8^-] = [\text{H}^+] [\text{Perox}]_T / K_2 \quad (7)$$

is the total analytical concentration of peroxodiphosphate. A rate law deduced on the basis of these reactive species would show hydrogen ion dependence as found.

Copper(II) forms a complex with peroxodisulfate as reported in the oxidations of hydrazine^{10,11} and oxalate,¹² and since

Table V. Copper(II)-Catalyzed Oxidation of Iodide with Peroxodiphosphate: Plot of k_{obsd} vs. $[\text{Cu}^{\text{II}}]^2$ ($I = 0.5 \text{ M}$)

T/°C	$10^3(k_1'[\text{I}^-] + k_2')/\text{s}^{-1}$ from plot	$10^3 k_0/\text{s}^{-1}$ from uncatalyzed reactn	$10^{-5} k_c'/\text{M}^{-1} \text{ s}^{-1}$
30	6.9		26
35	13.2	9.0	38
45	24	21.5	65

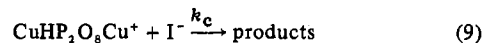
Table VI. Copper(II)-Catalyzed Oxidation of Iodide with Peroxodiphosphate: Plot of $k_{\text{obsd}}[\text{H}^+]$ vs. $[\text{H}^+]^2$ ($I = 0.5 \text{ M}$)

T/°C	$10^3(k_1'[\text{I}^-] + k_2')/\text{s}^{-1}$ from plot	$10^3 k_0/\text{s}^{-1}$ from uncatalyzed reactn	$10^{-5} k_c'/\text{M}^{-1} \text{ s}^{-1}$
30	7.3		24
35	8.7	9.0	42
45	20	21.5	75

peroxodiphosphate has the same structure, a complex formation is possible in the present case too. Kinetically it is not indicated, but the spectrophotometric results (Figure 1) show that the absorption pattern of the mixture is different from that of copper(II) or peroxodiphosphate. It may also be mentioned that if concentrated solutions of peroxodiphosphate and copper(II) are mixed in the absence of any acid, a light blue precipitate is obtained, which has copper(II) and peroxodiphosphate in the ratio 2:1. A point of interest to be noted is that the order in Cu^{II} is about 2 in the present reaction and was 2 also in the peroxodisulfate oxidation^{10,11} of hydrazine. Thus, a complex as shown in eq 8 appears to be formed prior



to the rate-determining step. The formation of a complex, $\text{CuHP}_2\text{O}_8^-$, preceding step 8 is also not ruled out. A reaction of $\text{HP}_2\text{O}_8^{3-}$ (with three negative charges) with Cu^{2+} appears to be more probable than reaction of $\text{H}_3\text{P}_2\text{O}_8^-$ or $\text{H}_2\text{P}_2\text{O}_8^{2-}$ with Cu^{2+} . In any case, in acid medium, the concentration of the complex would be small as compared to total Cu^{II} since the concentration of $\text{HP}_2\text{O}_8^{3-}$ is small in the acid medium employed and the stability constant of the complex is likely to be small since complexation is not indicated kinetically. The rate dependences show that the rate-determining step is (9).



The complex rate law, including step 9 and the rate from the uncatalyzed reaction,⁵ is

$$-d[\text{Perox}]/dt = k_1[\text{H}_3\text{P}_2\text{O}_8^-][\text{I}^-] + k_2[\text{H}_3\text{P}_2\text{O}_8^-] + k_c[\text{CuHP}_2\text{O}_8^+][\text{I}^-] \quad (10)$$

or

$$k_{\text{obsd}} = \frac{[\text{H}^+]}{K_2} (k_1[\text{I}^-] + k_2) + k_c K_3 K_7 [\text{Cu}^{\text{II}}]^2 [\text{I}^-] / [\text{H}^+] = [\text{H}^+] (k_1'[\text{I}^-] + k_2') + k_c' [\text{Cu}^{\text{II}}]^2 [\text{I}^-] / [\text{H}^+] \quad (10)$$

At constant $[\text{H}^+] = 0.1 \text{ M}$ and $[\text{I}^-] = 0.1 \text{ M}$, the plot of k_{obsd} vs. $[\text{Cu}^{\text{II}}]^2$ yields a straight line with an intercept. Table V gives the values of ($k_1'[\text{I}^-] + k_2'$) and k_c' . k_0 values of the uncatalyzed reaction are also included for comparison.

For hydrogen ion dependence at fixed $[\text{I}^-]$ eq 10 can be written as (11). A plot of $k_{\text{obsd}}[\text{H}^+]$ vs. $[\text{H}^+]^2$ would yield

$$k_{\text{obsd}}[\text{H}^+] = [\text{H}^+]^2 (k_1'[\text{I}^-] + k_2') + k_c' [\text{Cu}^{\text{II}}]^2 [\text{I}^-] \quad (11)$$

a straight line from the slope and intercept of which ($k_1'[\text{I}^-]$

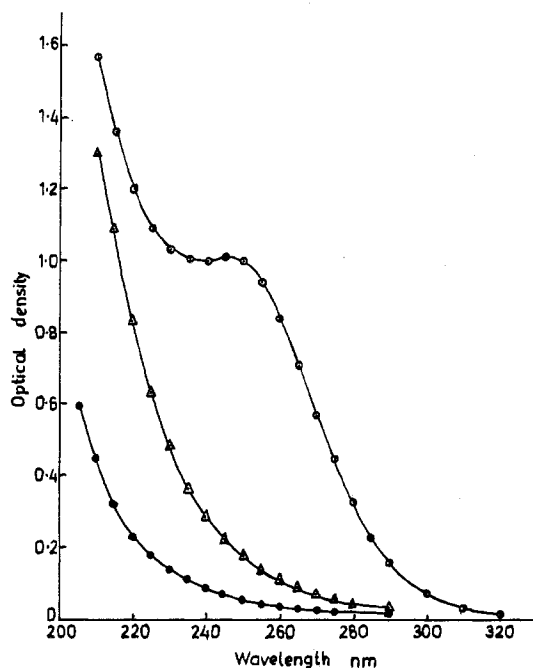


Figure 1. Optical measurements: (Δ) 0.001 M CuSO_4 ; (\bullet) 0.001 M $\text{K}_4\text{P}_2\text{O}_8$; (\circ) 0.001 M CuSO_4 and 0.0005 M $\text{K}_4\text{P}_2\text{O}_8$.

+ k_2') and k_c' can be calculated. Again the values of ($k_1'[\text{I}^-] + k_2'$) and k_0 are similar. Another fact to be noted is the similar values of k_c' from the two different plots (Table VI).

For iodide dependence, eq 10 can be written as (12). Thus,

$$k_{\text{obsd}} = [\text{I}^-] (k_1' [\text{H}^+] + k_c' [\text{Cu}^{\text{II}}]^2 / [\text{H}^+]) + k_2' [\text{H}^+] \quad (12)$$

a plot of k_{obsd} vs. $[\text{I}^-]$ would yield a straight line with an intercept. The values of k_2' and slopes have been given in Table VII. Values of k_2' from the uncatalyzed reaction are also given for comparison. Again the agreement in the values of k_2' is satisfactory.

The overall energy of activation calculated from the earlier paper⁵ was found to be $14.4 \pm 0.7 \text{ kcal mol}^{-1}$. The value found in the present work is $11 \pm 2.3 \text{ kcal mol}^{-1}$. Thus, the main function of copper(II) seems to be to lower the energy barrier by complex formation, but there is no evidence for a $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ cycle in the present reaction. In the operation of this cycle one of the two steps, either the reduction of Cu^{II} or the oxidation of Cu^{I} , should be rate determining. In the former case the rate, by and large, should be independent of the oxidant concentration. In the latter case the rate should be independent of the iodide concentration. Since neither of the two situations is met with and also since the oxidation of Cu^{I} with per-

Table VII. Copper(II)-Catalyzed Oxidation of Iodide with Peroxodiphosphate: Plot of k_{obsd} vs. $[\text{I}^-]$ ($I = 0.5 \text{ M}$)

$T/^\circ\text{C}$	$10^4 k_2' / \text{M}^{-1} \text{s}^{-1}$ from plot	$10^4 k_2' / \text{M}^{-1} \text{s}^{-1}$ from uncatalyzed reactn	slope from plot	slope calcd
30	7.5		11.3×10^{-3}	
35	12.5	8.3	12.5×10^{-3}	9.8×10^{-3}
45	20	20	26.5×10^{-3}	21.1×10^{-3}

oxodiphosphate appears to be quite fast, it appears probable that the $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$ cycle does not operate in this case. Studies of the kinetics of copper(II)-iodide reaction and copper(I)-peroxodiphosphate reaction can throw further light on the mechanism of this reaction.

A look at Table II shows that the nature of the effect of hydrogen ion on the rate depends on the concentration of copper(II). For larger concentrations of copper(II) this effect is irregular. Such behavior is quite expected from the hydrogen ion dependence shown in the rate law (10) and has been found also in the oxidations of Fe^{II} with vanadium(V),¹³ of Fe^{II} with cerium(IV),¹⁴ and of Sb^{III} with cerium(IV).¹⁵ If k_{obsd} values are calculated for different concentrations of the reactants and compared with those observed, the agreement is more than satisfactory considering the complex nature of the reaction.

Phosphate ion radical, PO_4^{2-} , has been reported¹⁶ in the oxidation of Fe^{II} complexes and in the photolytic oxidation¹⁷ of water, but no such evidence was found in the present investigation (absence of any effect of acrylamide on the rate).

Registry No. Perox, 15538-83-7; I^- , 20461-54-5; Cu^{II} , 15158-11-9.

References and Notes

- (1) S. Kapoor and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 473 (1976).
- (2) L. M. Bharadwaj, D. N. Sharma, and Y. K. Gupta, *Inorg. Chem.*, **15**, 1695 (1976).
- (3) S. Kapoor and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **39**, 1019 (1977).
- (4) A. Indelli and P. Bonora, *J. Am. Chem. Soc.*, **88**, 924 (1966).
- (5) L. M. Bharadwaj, D. N. Sharma, and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **39**, 1621 (1977).
- (6) S. Kapoor, P. D. Sharma, and Y. K. Gupta, *Talanta*, **22**, 765 (1975).
- (7) A. A. Green, J. O. Edwards, and P. Jones, *Inorg. Chem.*, **5**, 1858 (1966).
- (8) M. M. Crutchfield and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 3533 (1960).
- (9) M. Venturini, A. Indelli, and G. Raspi, *J. Electroanal. Chem. Interfacial Electrochem.*, **33**, 99 (1971).
- (10) A. P. Bhargava, R. Swaroop, and Y. K. Gupta, *J. Chem. Soc. A*, 2783 (1970).
- (11) R. Swaroop and Y. K. Gupta, *Indian J. Chem.*, **9**, 361 (1971).
- (12) M. Kimura, *J. Phys. Chem.*, **77**, 1265 (1973).
- (13) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **67**, 1090 (1963).
- (14) M. G. Adamson, F. S. Daiton, and P. Glentworth, *Trans. Faraday Soc.*, 689 (1965).
- (15) S. K. Mishra and Y. K. Gupta, *J. Chem. Soc. A*, 260 (1970).
- (16) A. A. Green, J. O. Edwards, and P. Jones, *Inorg. Chem.*, **7**, 170 (1968).
- (17) G. Bida, R. Curci, and J. O. Edwards, *Int. J. Chem. Kinet.*, **5**, 859 (1973).